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# DEGRADATION OF MUSTARD ON CONCRETE: GC/MSD AND SSMAS

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**14. ABSTRACT**
The products formed from the degradation of mustard [bis(2-chlorethyl) sulfide] on concrete were identified using gas chromatography with mass spectrometry detection (GC/MSD), $^{13}C$ solid state magic angle spinning (SSMAS) NMR, 1-D $^{1}H$ NMR, and 2-D $^{1}H$-$^{13}C$ NMR. In situ and extraction experiments were performed. Mustard was detected in the in situ SSMAS samples after a period of 12 weeks, whereas less than 5% of the mustard was detected in extracts from the concrete monoliths after 8 days. Sulfonium ions and (2-chloroethylthio) ethyl ether (T) were observed on the in-situ samples after a period of 12 weeks, whereas vinyl species and bis(2-chlorethyl) sulfoxide were observed in the extracts of the concrete monoliths within 24 hr. The sulfonium ion products formed by mustard on concrete had been previously observed in aqueous solution and wet soil. The vinyl products had been previously observed on metal oxides. Sulfoxide products had been identified in reactions with bleach, but T had not been observed in any of the prior systems.

**15. SUBJECT TERMS**

| | | | |
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| Mustard | Blister Agent | Bis(2-chloroethyl) sulfide | GC/MSD |
| $^{13}C$ NMR | SSMAS | Sulfonium ions | |

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DEGRADATION OF MUSTARD ON CONCRETE:
GC/MSD AND SSMAS

## 1. INTRODUCTION

Knowing when a Chemical Warfare Agent (CWA) no longer poses a hazard and a contaminated area is safe to enter without protective clothing are major concerns for battlefield commanders. Decisions must be made whether to decontaminate an area, or allow resumption of normal operations after an acceptable waiting period. The correct assessment of the amount of agent in the air, in nearby water, on equipment, and on the ground (substrates such as soil, grass, concrete and asphalt) is critical to making correct decisions about the need for decontamination. Therefore, testing methods that detect both the CWA and its degradation products, some of which may be toxic, are needed.

The chemistry of decontamination has been studied and reviewed.[1] Attention was paid to the presence of the CWA as well as to the quantity and identity of the breakdown products.

Previous studies demonstrated that the products formed after decontamination of mustard depended upon the method used. Bleach and other solutions and mixtures containing the hypochlorite ion, OCl-, were used as general decontaminants. These decontaminants reacted with mustard to form sulfoxide derivatives, which then formed sulfone derivatives, which then formed the corresponding elimination products.

Elimination products were seen immediately with the use of DS2, an alternative decontamination solution that was developed to avoid the corrosiveness of bleach. DS2 contained $CH_3\text{-}OCH_2CH_2O^-$ (2-methoxy ethanolate) as the active species; this basic ion reacted with mustard to form the elimination products 2-chloroethyl vinyl sulfide (CEVS) and divinyl sulfide (DVS).[2]

Reactions of mustard with water have also been studied. Although mustard exhibited low solubility in water, forming droplets within it, reactions occurred at the water-mustard interface to form the hydrolysis products chlorohydrin (CH) and thiodiglycol (TDG), which subsequently formed the sulfonium ions H-2TG and CH-TG (Figure 1).[2]

Reactions of mustard in solid matrices have also been studied. Wagner and MacIver[3] used $^{13}C$ SSMAS (solid state magic angle spinning) NMR to show that mustard persisted for several weeks on dry soil, but hydrolyzed and polymerized to form toxic CH-TG and H-2TG within 1 week when water was added. Environmentally, mustard has been observed to persist for 4 years in soil.[4]

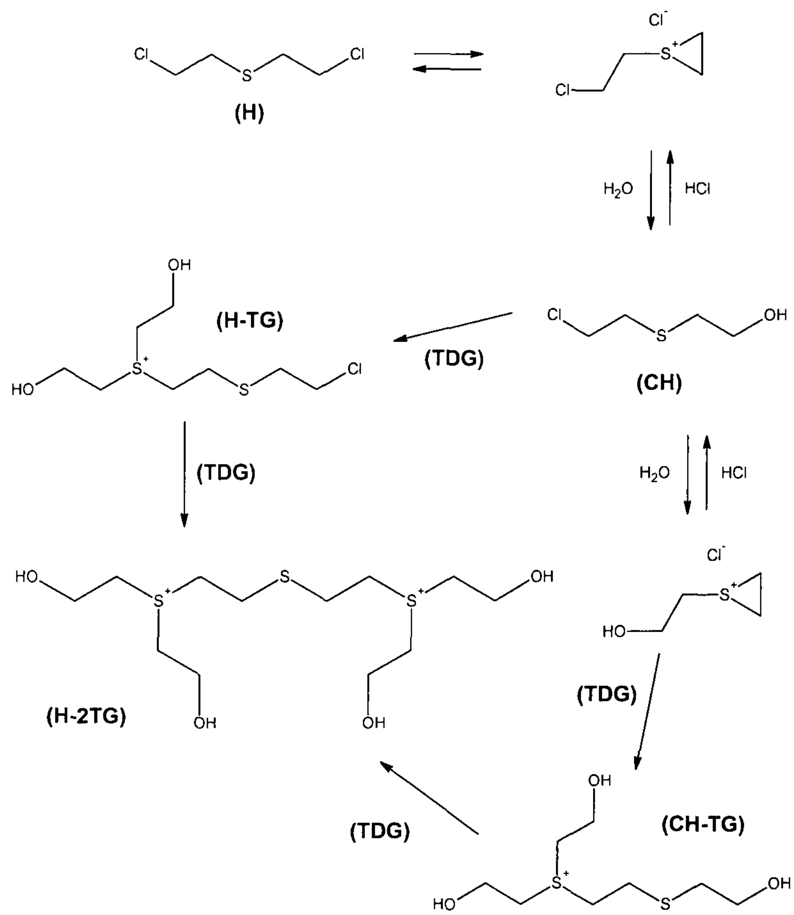


Figure 1. (Scheme 1) Reactions of Mustard with Water.

The reactions of mustard on MgO, CaO and $Al_2O_3$ metal oxide powders have also been studied using $^{13}C$ SSMAS NMR. When mustard was placed on MgO or CaO, the products thiodiglycol (TDG), CEVS and DVS were formed.[5] Degradation of mustard on CaO also led to minor amounts of sulfonium ions.[6] On the surface of ambient alumina, mustard reacted to give mostly thiodiglycol with minor amounts of CEVS and DVS (Figure 2). When excess water was added, the sulfonium ions H-2TG and CH-TG were formed, and $Al(H_2O)_6^{3+}$ was liberated from the surface.[7] The product distribution varied based on the degree of hydration and particle size of the metal oxide; but in general, elimination products were the most prevalent.

SSMAS was not the only method used to study reactions of mustard in solid matrices; the extraction method was also commonly used. CWAs and their degradation products were removed from solid matrices using solvents and then analyzed.[8] Davis et al.[9] extracted mustard from concrete after a 30-min contact time using isopropanol and acetonitrile; gas chromatography with mass spectrometry (GC/MS) analysis of the solvent showed 2 to 68% recovery of mustard when isopropanol was used and 7 to 21% recovery of mustard when acetonitrile was used. Decomposition products were not detected. Tomkins et al.[10] developed an extraction and GC method for analyzing the breakdown products of mustard on soil and concrete. The substrates were spiked and extracted immediately; the percent recovery of the analytes from the substrates ranged from 87 %to 122%. Wils et al.[11] used thermal desorption followed by headspace analysis to monitor the recovery of mustard from rubber over a period of 6 weeks. The 30-min recovery was 86%; the 6-week recovery was 57%.

In the current study, both extraction and SSMAS techniques were employed to study the persistence and reactivity of mustard on concrete quantitatively. The mustard and its degradation products were extracted from concrete monoliths with chloroform and analyzed using both GC/MSD and liquids NMR. For the SSMAS studies, a sample of mustard on the same concrete was sealed in a SSMAS rotor and monitored over a period of 12 weeks. In addition, mustard was placed onto concrete, which was then crushed, studied using SSMAS, and subsequently extracted for GC/MSD; this procedure enabled side-by-side comparison of the SSMAS and extraction methods.

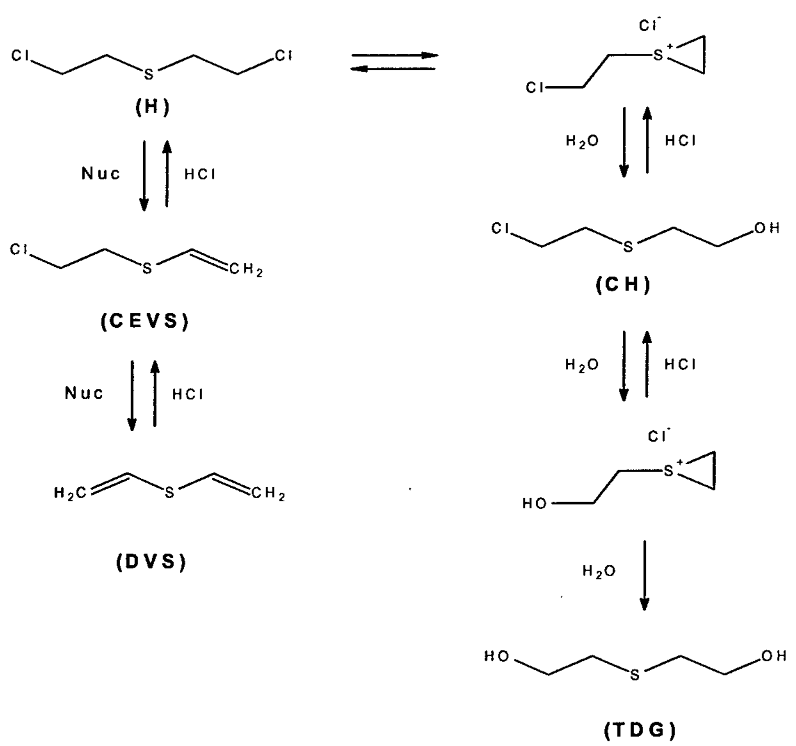


Figure 2. (Scheme 2) Reactions of Mustard on Metal Oxide Surfaces.

## 2. EXPERIMENTAL PROCESS

### 2.1 Substrates.

The concrete was made in the year 2000 using Portland cement, ~3 mm silicate filler, and a 0.32 water to concrete ratio. All samples were used under ambient conditions (about 21 °C and 20% RH). The concrete had a surface area of 7.8 $m^2/g$ and 17% porosity (4 samples) as measured by Mercury Intrusion Porosimetry (MIP). Nitrogen Gas Adsorption with BET surface area (SA) calculations gave a value of 9.0 $m^2/g$ for a small monolith. A concrete sample, which had been finely ground with mortar and pestle, had a surface area of 6.3 $m^2/g$, thus indicating that some pores were destroyed during the grinding process. The MIP and SA data were collected by Micromerities Inc. (Norcross, GA).

### 2.2 Agent.

Two different sources of mustard were used. The first was munitions grade (H) shown to be 85% pure by GC/MSD. The second was $^{13}C$ labeled HD*, which was amber-colored and shown to be 99.5% pure by GC. Both were supplied by Mr. David Sorrick. The HD* was 50% labeled at each carbon position, such that two $^{13}C$ would not be adjacent. This allowed for good detection of the $^{13}C$ signal, but avoided the $^{13}C$-$^{13}C$ couplings that would be present if 100% labeling were used. **Caution: mustard, bis(2-chloroethyl) sulfide is a potent vesicant, and care must be taken to prevent exposure to liquid or vapor. It should only be manipulated by trained personnel employing appropriate engineering controls and personal protective equipment.**

### 2.3 Extractions.

Four 1-µL drops of mustard ($(ClCH_2CH_2)_2S$) weighing approximately 6 mg total, were placed onto monoliths of ambient concrete that were about 3 mm thick, 15 mm long, and 9 mm wide. Typical concrete samples weighed 1.3 g (concrete/mustard ratio = 220 : 1) although experiments with 0.3 g and 0.6 g monoliths were also performed (concrete/mustard ratios of 50 : 1 and 100 : 1 respectively). The concrete samples were stored in 20-mL glass vials that were sealed with GC septum caps. After a specified exposure time at 21 °C the samples were crushed in the vial using pliers, and extracted once with 2-mL $CDCl_3$. The extracts were analyzed using GC/MSD and liquids $^1H$ NMR. Typical mustard concentrations in solution were 2 mg/mL. All concrete samples were made in duplicate; the NMR and GC/MSD of the extracts were run once.

### 2.4 NMR Instrumentation.

$^1H$ NMR liquids spectra were collected at 9.4 Tesla using a Varian Inova NMR spectrometer equipped with a Varian 5-mm liquids probe. All spectra were obtained using direct polarization; delay times between pulses were at least 5 times the measured $T_1$, and the chemical shift reference was internal chloroform. Quantification of the mustard extracted was obtained by comparing total integrated peak areas between an external standard that was approximately

2-mg/mL mustard in chloroform and the extract. The vinyl compounds 2-hydroxyethyl vinyl sulfide (HOEVS, 5.35 and 6.45 ppm) and 2-chloroethyl vinyl sulfide (CEVS, at 5.22 and 6.28 ppm) were detected by $^{1}H$ NMR; quantification was based upon the vinyl resonance at ~5.3 ppm. The aliphatic protons were observed as small peaks adjacent to the much larger mustard resonances.

$^{13}C$ SSMAS spectra were collected at 9.4 Tesla using a Varian Inova NMR spectrometer equipped with a Doty Scientific 7-mm standard series VT-MAS (variable temperature magic angle spinning) probe. The spectra were obtained using direct polarization at spinning rates of ~2000 Hz. Delay times between pulses were at least 5 times the measured $T_1$, and spectra were referenced to external tetramethylsilane. Alternatively, the $^{13}C$ SSMAS spectra were measured at 7.0 Tesla using a Varian Inova NMR spectrometer equipped with a Doty Scientific 7 mm high-speed VT-MAS probe and spinning at 3000 Hz.

Two-dimensional COSY, HMBC and HMQC spectra were collected at 25 °C at 14.1 Tesla using a Varian Inova NMR spectrometer equipped with a Varian 5 mm 'HCN' indirect detection liquids probe, and the chemical shift reference was internal chloroform. The pulse sequences used were those supplied by the manufacturer. Typical parameters for the HMQC experiment were: 32 transients, 128 increments of the $t_1$ evolution period, scalar coupling constant of 144 Hz, and a recycle time of 1.5 s. Typical parameters for the HMBC experiment were 96 transients, 256 increments of the $t_1$ evolution period, scalar coupling constant of 144 Hz, long-range spin coupling constant of 7 Hz, and a recycle time of 1.5 s. Typical parameters for the COSY experiment were 16 transients, 512 increments of the $t_1$ evolution period, and a recycle time of 2 s.

### 2.5 GC Instrumentation.

An Agilent Technologies 6890 Series gas chromatograph equipped with a 5973 mass selective detector (MSD) was used for all mass spectral analyses. Ultra-Pure helium (99.999%) was used as the carrier gas with an average linear velocity of 36 cm per s in the splitless-constant flow mode. The inlet temperature was 250 °C, the inlet mode was splitless (purge on at 0.1min, flow 50mL/min), the inlet pressure was 7.3 psi (constant flow at 1 mL/min), and a 1-µL sample volume was used. The oven temperature profile was 45 °C for 5 min, then increasing to 250 °C at the rate of 10 °C/min with no final hold time. The GC column was an HP-5MS, 30-m X 0.25-mm X 0.25-µm film thickness. The mass range for the MSD was 40 to 350 amu. The mustard was 85% pure (retention time 13.32 min); Q (1,2-bis(2-chloroethylthio) ethane, $ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$, 20.05 min) was a major impurity, present at about 11% of the total. 1,4-dithiane ($C_4H_8S_2$, 11.32 min) was present at 2.6%; all other impurities, including $S_8$, were present at less than 1% by GC area. The GC data were considered semi-quantitative since standards were not available for the products; the percent products were calculated by normalizing to the amount of mustard present in the standard. The products found in the GC (retention time, minutes) were 2-chloroethyl vinyl sulfide (CEVS, 7.92), 2-hydroxyethyl vinyl sulfide (HOEVS, 8.34), 1,2-bis vinylthio ethane (BVTE, $CH_2{=}CHSCH_2CH_2SCH{=}CH_2$, 13.02), and (2-chloroethylthio)ethyl vinyl sulfide (CETEVS, $ClCH_2CH_2SCH_2CH_2SCH{=}CH_2$, 16.74).

## 3. RESULTS

### 3.1 Extraction of Mustard from Concrete Monoliths.

Contact Time : When the samples were extracted after 1 hr, the percentages of mustard recovered were 90% to 100%. The NMR and GC percent recoveries were generally within 10% of each other for any given extract; sample-to-sample variation of the duplicates was also generally within 10%. As the contact time of mustard on concrete was increased, the percent mustard extracted decreased; about 40% of the mustard was extractable after 24 hr (Figure 3). The concrete/mustard ratio for these samples was 220 : 1.

Products were observed after a 24-hr contact time by using both NMR and GC/MSD. The CEVS and HOEVS products (Figure 4)were quantified by using $^{1}$HNMR. The GC/MSD was not quantitative for the products since standards were not available. CEVS and/or HOEVS were present in all of the samples that gave products; a variety of other compounds were occasionally detected. Compounds that were detected in some, but not all samples were bis(2-chloroethyl) sulfoxide, TDG, chlorohydrin (CH), and (2-hydroxyethylthio)ethyl ether ($(HOCH_2CH_2SCH_2CH_2)_2O$. These products were identified using 2-dimensional $^{1}H$-$^{13}C$ NMR and GC/MSD because the product chemical shifts in the 1-D $^{1}H$ NMR were too close to the much more intense mustard peaks for good identification. The sum of products and reactant extracted was less than 100% after a 24-hr contact time based on the $^{1}H$ NMR data.

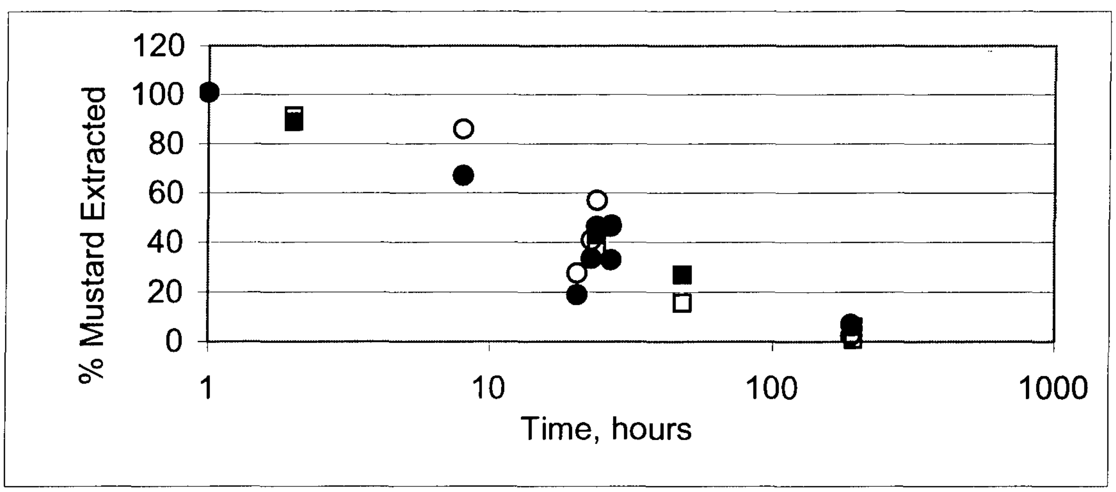


Figure 3. Percent Mustard Extracted from Concrete as a Function of Contact Time (Concrete/Mustard Ratio = 220 : 1 ● H via NMR; ○ H via GC; ■ HD* via NMR; and □ HD* via GC).

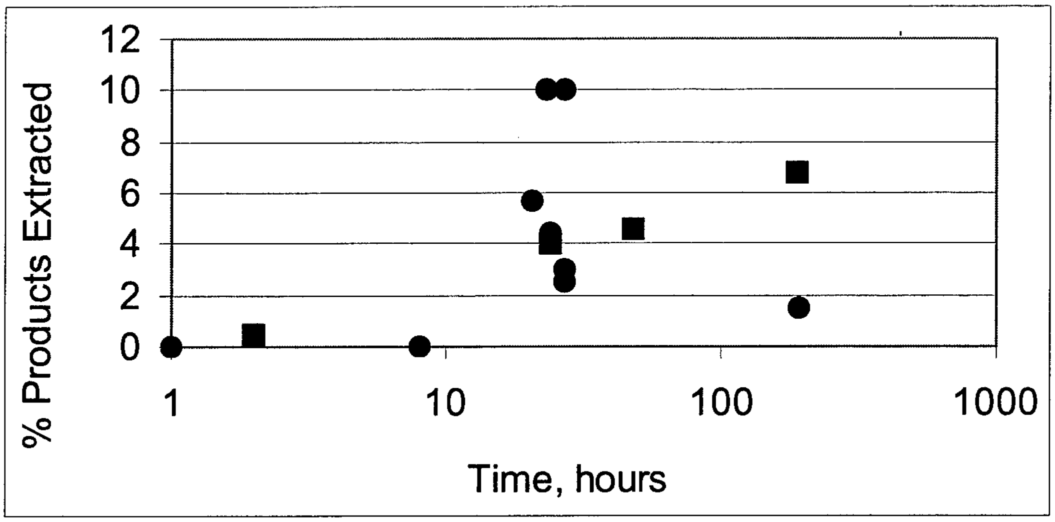


Figure 4. [1]H NMR Measurement of Percent Products Extracted from Concrete as a Function of Contact Time (Concrete/Mustard Ratio = 220 : 1. ● H; ■ HD*).

3.2 Concrete/Mustard Ratios.

The concrete/mustard ratios varied from 50 : 1 to 250 : 1; at a ratio of 50 : 1, the concrete was almost saturated with mustard. Extractions were performed after 24 and 192 hr. The percent mustard extracted after 24 hr remained relatively constant at ~50% regardless of the concrete/mustard ratio; after the 192-hr contact time the percent mustard extracted decreased from ~40% to ~5% as the ratio increased from 47 : 1 to 234 : 1 (Figure 5).

In addition to the mustard, the vinyl compounds 2-hydroxyethyl vinyl sulfide (HOEVS) and 2-chloroethyl vinyl sulfide (CEVS) were detected by [1]H NMR. Both vinyl species were seen in the 24-hr concrete/mustard ratio of 198 : 1 sample, and in all of the 192-hr contact time samples. Only CEVS was seen in the 24-hr samples with concrete/mustard ratios of 55 : 1 and 77 : 1.

The products identified by GC/MSD were CEVS, HOEVS, 1,2-bis vinylthio ethane (BVTE), and (2-chloro-ethylthio)ethyl vinyl sulfide (CETEVS) (Table). The relative amounts of product present (Table) were based on the normalized responses of the compounds in the GC to mustard; since standards were not available, it was not possible to quantify the products. The GC data showed that the amount of mustard decreased with contact time, the relative amount of products increased, and the impurities remained constant. The occurrence of the products depended upon the concrete/mustard ratio. After a 24-hr contact time, CEVS was formed when only a small amount of surface was available for the mustard (55 : 1), whereas HOEVS was produced when more surface area was available (77 : 1 and 198 : 1). Comparison of the products after 24-hr and 192-hr contact times also showed that CEVS formed first, followed by HOEVS. Thus, the elimination occurred before the hydrolysis. Divinyl sulfide (DVS) was not seen. CETEVS and BVTE, which both contain 2-sulfur atoms, were likely formed by the degradation of Q on the concrete.

Table. Products and the Normalized Response Observed in the Extracts of Different Concrete/Mustard Ratio Samples via GC/MSD.

| Products and the normalized response observed via GC/MSD | 24-hr concrete/mustard ratio | | | 192-hr concrete/mustard ratio | | |
|---|---|---|---|---|---|---|
| **Concrete/Mustard Ratio** | **55:1** | **77:1** | **198:1** | **47:1** | **86:1** | **234:1** |
| 2-Chloroethyl vinyl sulfide, CEVS | 2.3 | 3.3 | 4.0 | 1.3 | 3.7 | 4.9 |
| 2-Hydroxyethyl vinyl sulfide, HOEVS | | 0.3 | 1.7 | 0.1 | 0.4 | 5.8 |
| 1,2-Bis(vinylthio) ethane, BVTE | | | 0.6 | | 0.5 | 1.7 |
| (2-Chloroethylthio)ethyl vinyl sulfide, CETEVS | | | | 3.1 | 4.3 | 8.8 |

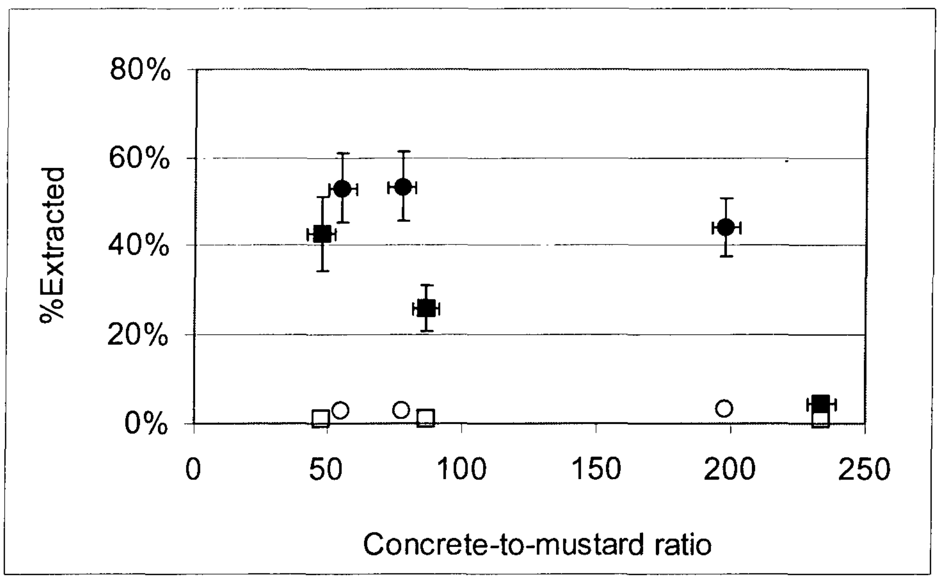


Figure 5. Percent Mustard and Vinyl Products Extracted from Concrete as a Function of Concrete/Mustard Ratio (● H after 24 hr; ○ vinyl products after 24 hr; ■ H after 192 hr; □ vinyl products after 192 hr).

3.3 SSMAS Studies.

$^{13}C$-labeled mustard was placed onto finely ground concrete (concrete/mustard ratio = 40 : 1) and sealed in a rotor for SSMAS experiments. Initially, numerous spinning sidebands were observed for the HD* on the concrete (Figure 6). However, after 12 weeks, very few spinning side bands were seen; the total integrated peak area had gradually decreased to 60% of its original value; and the peak widths had increased from 200 Hz to 500 Hz (Figure 7). The chemical shifts of mustard, at 34.1 and 43.4 ppm were unchanged during this process.

The final spectrum was acquired with a 1-s recycle time. This experiment was performed based on the observation that the $T_1$ became shorter for products on a different concrete. The short recycle time had the net effect of enhancing the intensity of any short-$T_1$ product peaks relative to the longer $T_1$ background and reactant peaks (Figure 8). The total integrated peak area was larger than observed in the initial spectrum, due to the fact that the shorter $T_1$ affected the baseline on which the integral was calculated.

In addition to the mustard peaks, the spectrum had peaks at 19.3, 57.3, and 72.2 ppm that were about 500 Hz wide, and shoulders at 29.5 and 48.8 ppm. The chemical shifts at 29.5, 48.8, and 57.3 were consistent with the presence of the sulfonium ion H-2TG; CH-TG has similar chemical shifts but has an additional peak at 62 ppm, which was not seen. Another product, (2-chloroethylthio)ethyl ether, (T, $ClCH_2CH_2SCH_2CH_2OCH_2CH_2SCH_2CH_2Cl$, the ether of 2 hydrolyzed mustard molecules) was identified by its peak at 72.2 ppm; its other resonances were at 43, 35, and 32 ppm, all of which were observed in the spectrum. The 19.3 ppm peak has not yet been identified. Thus, after 12 weeks, a combination of mustard, H-2TG, and T were present on the concrete.

## 3.4 Comparison between SSMAS Studies and Extractions.

The timescale progression of the SSMAS sample was compared to that of the extracted monoliths (Figure 9). After 192 hr, the amount of mustard that was detected in the extracts from the monoliths was approximately 5%, yet the SSMAS spectra showed no decrease in the percentage of mustard that was present. The mustard peak widths in the SSMAS sample increased from 200 Hz to 300 Hz over this period of time. Liquid mustard that was not interacting with a surface would demonstrate a peak width of 20 to 50 Hz under the same conditions. Thus, adsorption of the mustard to the surface may have begun within the 1-hr time frame that it took to acquire the initial spectrum, and continued with time, as evidenced by the increasing peak widths.

In order to further investigate the apparent dichotomy between the SSMAS and extraction results, a few monoliths were spiked with mustard, finely ground after the specified contact time, measured by SSMAS, and then extracted. The SSMAS total integrated peak areas were quantified by comparison to a freshly-made standard of mustard on finely ground concrete. The SSMAS and extraction data pairs were compared to the previously obtained extraction data of percent mustard extracted versus concrete/mustard ratio and the trend lines that joined those data (Figure 10).

At a concrete/mustard ratio of 91 : 1, and a 24-hr contact time, more mustard was seen in the SSMAS spectra than was extracted. However, when typical error bars of 15% were added to all of the data, the SSMAS and extracted data were seen to fall within the range of the previous extraction data for the 24-hr samples. The 192-hr sample at a concrete/mustard ratio of 77 : 1 exhibited more mustard in the SSMAS than was extracted even after considering the experimental error.

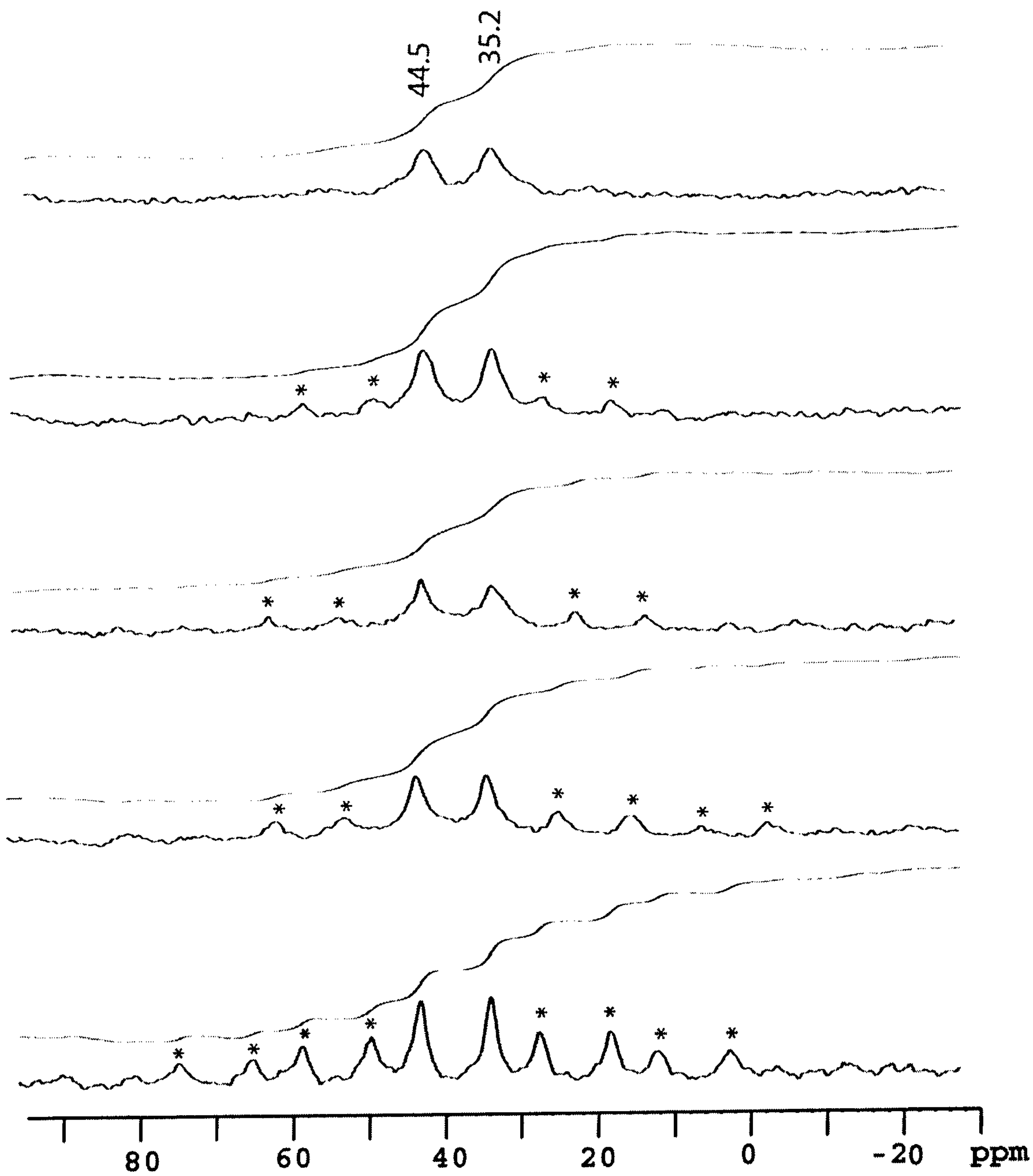


Figure 6. $^{13}C$ SSMAS Spectra of HD* on Concrete. (Age of spectra from bottom to top: initial, 2, 4, 7, and 12 weeks.)

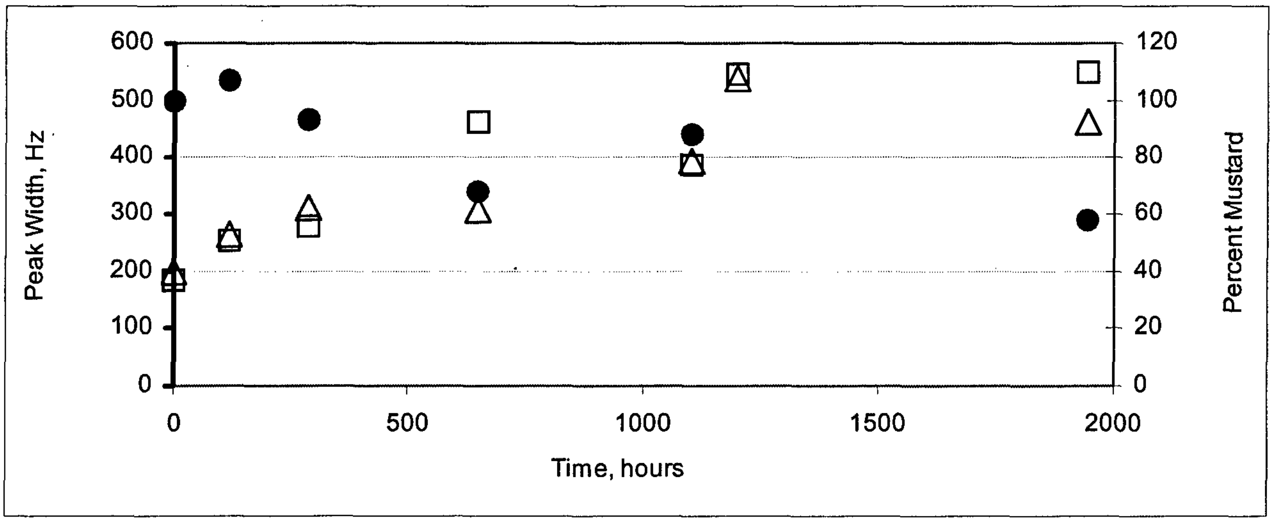


Figure 7. Summary of SSMAS Spectra of HD* on Crushed Concrete. (Left axis: peak widths at 35 ppm (□) and 44 ppm (△) in Hz. Right axis: normalized total integrated peak area for mustard (●) in percent.)

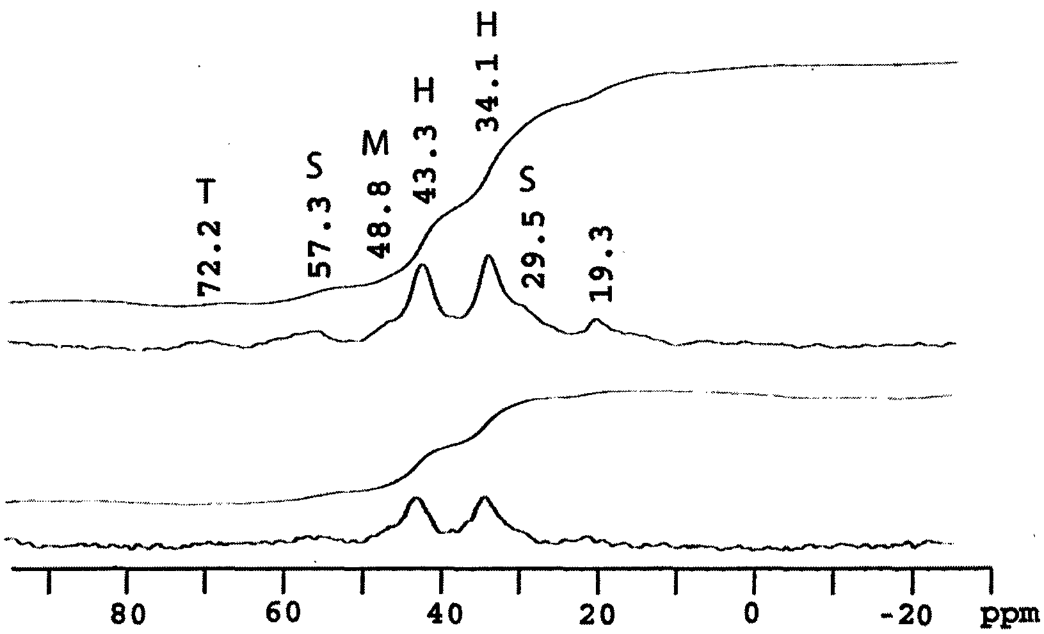


Figure 8. $^{13}C$ SSMAS Spectra of HD* on Concrete after 12 Weeks. (Recycle times: bottom - 10 s and top - 1 s. H represents mustard; T is for (2-chloroethylthio)ethyl ether; S is for sulfonium ion; and M represents multiple species.)

At a concrete/mustard ratio of ca. 155 : 1 and a 24-hr contact time the percent mustard observed by SSMAS and that extracted were very similar, 43% and 40% respectively. At a concrete/mustard ratio of ca. 155 : 1 the mustard was not detected in the SSMAS spectra after a 48-hr contact time, probably due to its low concentration and the numerous spinning side bands that were typical for this system. Only 4% of the original mustard was extracted.

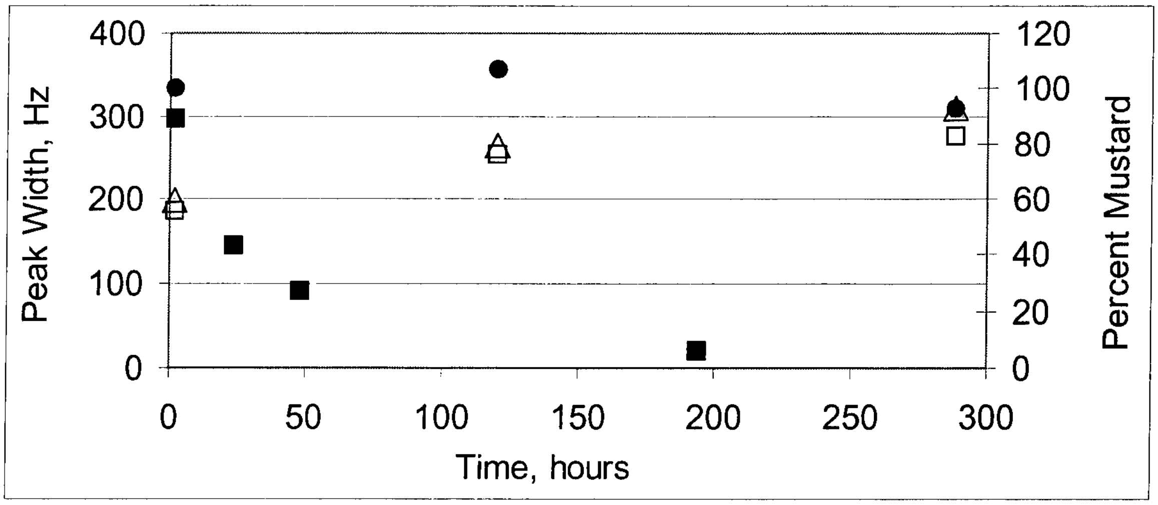


Figure 9. Comparison of SSMAS Spectral Data for HD* on Crushed Concrete with Extraction Data. (Left axis: peak widths at 35 ppm (□) and 44 ppm (△) in Hz. Right axis: percent mustard recovered from extraction (■) and normalized total integrated peak area for mustard via SSMAS (●).)

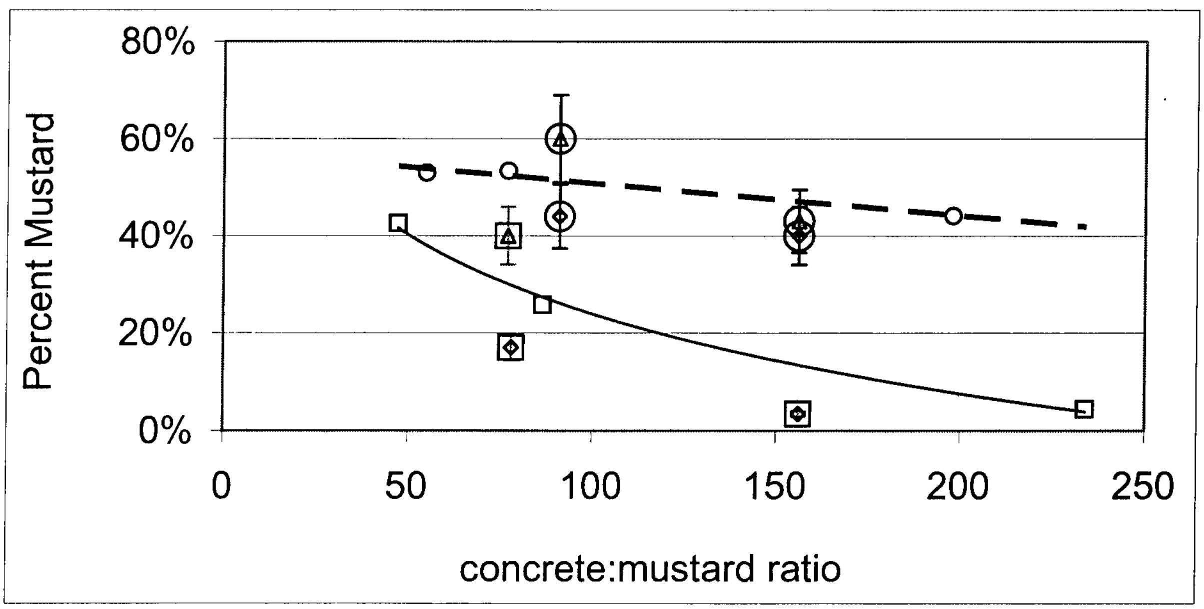


Figure 10. Percent Mustard Extracted after 24 Hr (○) and 192 Hr (□). (Percent mustard observed using SSMAS (△) followed by extraction (◇).)

## 4. DISCUSSION

The observed decline in the extraction efficiency of mustard from concrete as the contact time increased was similar to the trends seen in prior investigations. Beck et al.[12] used pressurized liquid extraction to remove thiodiglycol from 2 soils and 1 type of sand; their percentage recovery ranged from 56 to 89 after 24 hr depending upon the substrate, and declined over a period of 1 to 28 days.

The concrete/mustard ratio affected the rate of product formation. A concrete/mustard ratio of 170 : 1 corresponded to a monolayer of mustard coverage based on a mustard molecular [3] of 38 Å$^2$, a 1.3 g monolith with a surface area of 8.4 m$^2$/g spiked with 6 mg mustard. At a concrete/mustard ratio of 55 : 1 some of the mustard was not in contact with the concrete but in a more liquid-like state in the pores of the concrete. This mustard would be less reactive than that in contact with the concrete surface, and hence react more slowly.

The initial SSMAS measurements of mustard on ground concrete showed multiple spinning side bands; these indicated a high degree of order of the mustard on the concrete, and implied that the mustard was bound to the surface rather than remaining as mobile droplets within the matrix. Initially, the spinning side bands accounted for ~50% of the total peak intensity, and thus precluded use of higher concrete/mustard ratios in the SSMAS experiments (the use of 2 mg mustard with 200 mg finely ground concrete in the rotor would barely be above the detection limit). The continuous broadening of the peaks in the SSMAS spectra indicated that the mustard and its products were binding more tightly to the concrete over time. The peak width data were consistent with the observations that less mustard was extracted as the surface areas and contact times increased. These results were in contrast to the results in soil, in which the peaks remained narrow throughout the reaction.[3] Thus, the peak widths observed in this work were 200 Hz wide, compared to the 20 to 50 Hz peak widths that were typically seen for non-adsorbed liquid droplets in the SSMAS experiment.

Performing SSMAS experiments on monolithic samples that were spiked, aged, and then ground immediately prior to extraction indicated that approximately half of the mustard was not seen in the SSMAS spectra. The interpretation of this data was that the mustard adsorbed onto the concrete and bound to it more tightly with time, resulting in peaks that were too broad for detection. Grinding the sample simultaneously removed existing pores and created new surfaces onto which any liquid mustard could adsorb. As the mustard adsorbed onto and then bound with the concrete, the peaks broadened and thus became difficult to detect. Hence, only half of the mustard that was put onto the monolithic sample was detected in the SSMAS spectra. All of the mustard that was observed in the SSMAS after a 24-hr contact time was detected in extracts; the extractability decreased as the contact time increased to 192 hr.

The products observed depended upon whether extraction or SSMAS methods were used to detect the products. A combination of mustard, H-2TG and T were detected on finely ground concrete after a 12-week contact time by SSMAS. The data from the extracts of the monoliths showed ~3% elimination products after 1 week, with ~5% mustard remaining, and the bulk of the material was not detected. These results are consistent with a mechanism in which most of the mustard bound tightly to the concrete and reacted over a period of 12 weeks, eventually forming H-2TG and T. Approximately 5% of the mustard formed elimination products; S-oxidized products and hydrolysis products were only detected occasionally. Since small samples of a heterogeneous substrate were used, slight variations in the products detected were not surprising.

The elimination pathway proceeded via elimination first followed by hydrolysis, as evidenced by the order of appearance of CEVS and HOEVS in the Table. More HOEVS was present on the samples that had a higher concrete/mustard ratio; this result was consistent with the fact that a larger sample of concrete would have more surface adsorbed water than a smaller sample. The formation of T, which occurred via hydrolysis of mustard to chlorohydrin followed by dimerization (Figure 11) has not been seen in any other schemes for mustard degradation. The formation of H-2TG, according to Scheme 1 (Figure 1), required the hydrolysis of the mustard and the formation of TDG; yet TDG was only seen in 1 sample by GC/MSD and was not seen by NMR. This lack of detection of major amounts of TG and CH indicated that they reacted rapidly to form H-2TG or T. Consideration of the pathways for the formation of H-2TG indicated that at some point either H-TG and/or CH-TG must have been formed, yet they were not detected as isolated species.

The sulfonium ion products generated by the degradation of mustard on concrete indicated a similarity to the reaction in water and on wet soil. This was not surprising, since concrete is porous and hygroscopic, and in equilibrium with the environmental moisture present.

The elimination product CEVS indicated that the reaction also had a component similar to that seen on CaO, MgO and alumina, all of which formed elimination and hydrolysis products (TDG, CEVS and DVS). TDG and DVS were not seen on the concrete; formation of sulfonium ions from the TDG dominated the products. Elimination, hydrolysis and sulfoxide products were also detected in extracts of soil samples from the Iran-Iraq war.[13, 14]

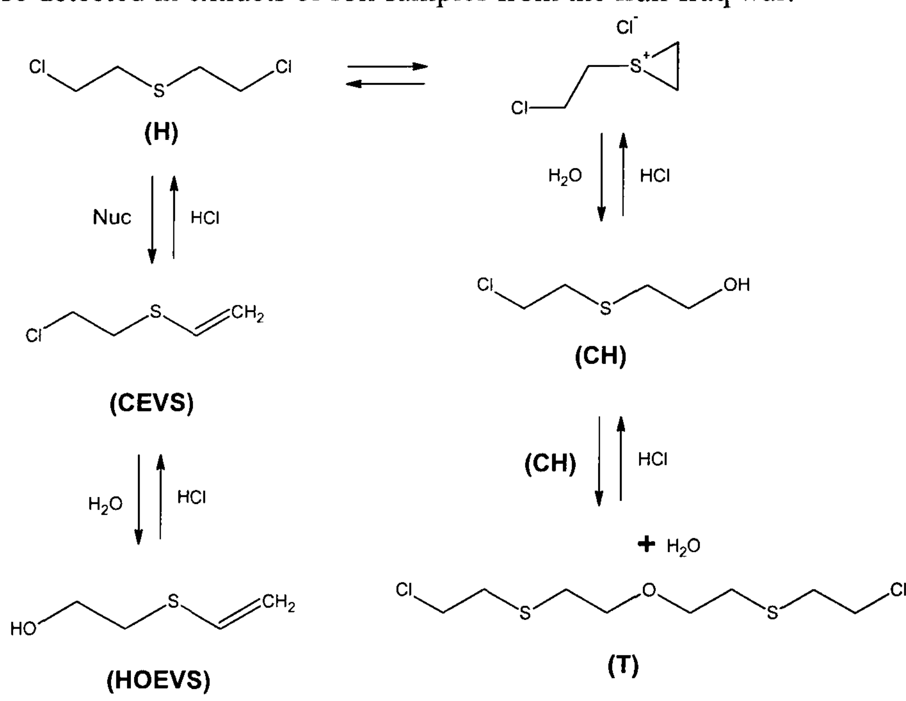


Figure 11. (Scheme 3) Formation of T in Concrete.

# 5. CONCLUSIONS

After 200 hr, very little mustard was extracted from the concrete monoliths, but the solid state magic angle spinning spectra of crushed samples showed clearly that it was still present. This difference suggested that the mustard existed in the concrete in a non-extractable form prior to its degradation.

The degradation progressed similarly to that in water or on wet soil yielding mostly sulfonium ion products, with a minor component of the reaction yielding elimination products as observed on metal oxides. In addition, the degradation on concrete yielded T, a product that had not been previously observed.

The formation of toxic H-2TG [3] from the decomposition of mustard demonstrated that measuring the disappearance of mustard from concrete is not sufficient to declare an area safe for re-entry and re-use. In order to declare an area safe for re-entry, the degradation products formed must be identified. Extraction methods alone are not sufficient; methods to identify the presence of non-extractable degradation products must also be used.

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